

New Way to Produce Magnetite Nanoparticles at Low Temperature

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Abstract

This work reports a simple process for preparation of stable and uniform magnetite nanoparticles (Fe_3O_4) at low temperature. The method is supported in three single steps and provides low-sized functionalized magnetite nanoparticles at lower temperatures than the obtained by similar methods. The samples have been characterized by x-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FT-IR), transmission electron microscopy (TEM), and vibrating sample magnetometry (VSM), where it shows the nature of the nanoparticles. This study reveals that these nanoparticles are spherical in shape and have an average size of 30 nm, they present a super-paramagnetic behavior, and IR spectra show the group of N-monosubstituted amides, CO-NH in the cover of the superparamagnetic nanoparticles which avoids their agglomeration..

Keywords

Magnetite Nanoparticles; Low Temperature Synthesis; Coated Magnetite; Oleic Acid Coating

Introduction

There are many ways to synthesize magnetic nanoparticles among which stand out the chemical coprecipitation [1-4], emulsion [5-8], pyrolysis [9], sol-gel [10], fluid injection [11], vaporization [12-14], hydrothermal [15-18], etc. In this sense, the interest in developing new methods to fabricate magnetic nanoparticles is given by the potential applications proposed and investigated in recent years, which involve many fields of technology [19]. In what concerns to biomedical applications it is important to highlight the use of nanoparticles for hyperthermia treatment of cancerous tumors, in which a tight control of preparation for the nanoparticles is indeed vital given the close relationship between their properties and the way in which nanoparticles are made.

Many research groups all over the world have attempted to synthesize, by various methods, the stable magnetic oxide nanoparticles such magnetite, obtaining various morphologies and size distributions. However, the drawback in these methods is the use of massive amounts of surfactants, complex and sophisticated equipment, and the high processing temperature [20].

A major concern in nanoparticles synthesis is control over size. In the case of magnetite, size copes the magnetic properties. Nanoparticles below a size threshold of 20 to 30 nm exhibit superparamagnetic behavior at room temperature. Above this threshold, in the range from 20 to 80 nm, the nanoparticles are stable single domain ferrimagnets, and to produce these kinds of magnetic nanoparticles generally methods that involve elevated temperatures are required [21].

Attempts to produce nanoparticles within the single stable domain by low temperature process in aqueous solutions have failed [22, 23]

Baumgartner et al, reported that controlling the pH tunes the growth of particles to the range of single stable domain using a low temperature co-precipitation of ferrous and ferric iron under alkaline conditions [24].

Some authors have developed synthesis routes using low temperatures, generally in the superparamagnetic range, thus very low grain size [20, 25-32]. Ye et al, used a solvent-free synthesis method induced at room temperature, this synthesis can be considered as a hybrid of solid-state reaction, co-precipitation and organic solution phase decomposition processes [33]. Awwad and Salem presented a facile, rapid and green method to prepare magnetite nanoparticles in one step reaction at relatively low temperature range 80-85°C [34]. Marquez et al reported one-step hydrothermal procedure without the use of surfactants or templates using temperatures about 120°C [35].

Recently, there are developed some alternative methods to synthesize high-quality magnetic nanoparticles. However, their obtaining is through a strict control of preparation parameters as temperature and pressure of an inert atmosphere. For example, by using hydrothermal methods is possible obtaining octahedral magnetite with high crystallinity at 90°C, which is very low temperature however, the average particle size is between 200-300 nm [36]. On the other hand, to obtain magnetite nanoparticles of 30 nm by hydrothermal synthesis, it is necessary higher temperature (160-200°C) as well long time to be prepared [37]. With this in mind, development of efficient methods to synthesize magnetic nanostructures with well-defined size distributions and shapes are one of the key trends in inorganic and physical chemistry.

It goes without saying that a very intensive investigation has been conducted to look for new strategies to prepare magnetic nanoparticles with tailor-made properties through appropriately attached functional moieties. In particular, for biomedical and contaminant removal applications, water-soluble nanoparticles are usually required. Then, to produce the nanoparticles is common to use the chemical coprecipitation technique from iron salts and the most recognized method was presented by R. Massart [38], however the magnetic nanoparticles produced by this method occur at, or above of 100°C, and greater dimensions than 100 nm are produced by preparing solutions containing [Fe (III)/Fe (II)], that may be coated with surfactants such as oleic acid or some other compounds, and heating above 100°C [38-40]. From the methodology developed in this work, is possible to obtain, not only hydrophobics, as those obtained previously, also hydrophilic magnetite nanoparticles [41, 42].

Nowadays, these nanoparticles are produced in such a way that their toxicity is low and they have been functionalized with proteins that human beings can tolerate [43]. Moreover, obtaining these nanoparticles was made more complicated and the simplicity proposed by Massart was lost.

Therefore, it is a synthetic challenge to develop new and optimize procedures already existent to obtain single stable domain particles under milder chemical conditions [20].

In this paper, we present a modification of the Massart's method which allows obtaining polydisperse magnetite nanoparticles in easy way at temperatures below 80°C, with a particle size that corresponds to the boundary between superparamagnetic and single stable domain behavior. This method may be divided into three simple stages easy to implement which allows satisfy to main objectives: i) synthesizing low-sized nanoparticles below of 100°C and ii) obtaining magnetite nanoparticles with a hydrophobic coating.

This kind of magnetic nanoparticles have applications in bio- and nanotechnology systems [19, 20, 44]. Magnetite nanoparticles in the boundary size of single to multi domains are produced by various organisms e.g., magnetotactic bacteria, birds and fishes, using these nanoparticles as sensors of geomagnetic field to aid their navigation [45]. In this sense, among the wide range of applications, biologists and geologists used the biomineralized magnetite nanoparticles as biomarkers to study current or fossil records [46, 47].

Materials and Methods

Reagents

For the preparation of the magnetite nanoparticles we used ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), ferrous chloride ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) and oleic acid ($\text{C}_{18}\text{H}_{34}\text{O}_2$) all of them of reagent degree. Also ammonium hydroxide (NH_4OH) at 28%, were used without any further purification. Ultrapure Milli-Q water (18.2) was used throughout the experiment.

Characterization

Infrared spectrum was obtained using an Avatar 360 FT-IR, x-ray patterns were obtained using a GBC-MMA

Diffraction MMA diffractometer with filtered $\text{CuK}\alpha$ ($\lambda = 1.54 \text{ \AA}$) radiation and MAUD program was used to refine the crystalline structure and corroborate the presence of magnetite. Micrographs were obtained from transmission electron microscopy at 100 kV using a JEOL-1230. The size particle was measured using a DLS Nanosizer, and the magnetic properties were determined using an Alternating Force Gradient (AGM) magnetometer with a maximum applied field of 10 kOe.

Experimental

The synthesis of magnetite nanoparticles was carried out at low temperatures in three simple stages, which are described below.

1) First Stage

One solution (s1) with 24.5 ml of ammonium hydroxide is dissolved in 200 ml of deionized water under stirring during 3 minutes. Then, the temperature increases a ratio of $3^\circ\text{C}/\text{min}$ until was reached 40°C , at this point, add 1.5 ml of oleic acid while stirring at 1050 rpm and temperature still increasing at $3^\circ\text{C}/\text{min}$ until it reaches 80°C .

2) Second Stage

Two solutions are prepared, one with 0.66 g of ferric chloride dissolved in 10 ml of deionized water (s2), and the other with 1.08 g of ferrous chloride dissolved in 20 ml of deionized water (s3). Both solutions are stirred, using a magnetic stir at 1050 rpm.

3) Third Stage

The (s1) is cooled from 80°C to 70°C while stirring at 1050 rpm, then (s2) and (s3) are slowly added to (s1) and then, the mix is newly heated to reach 80°C to form the magnetite nanoparticles. Once the magnetite nanoparticles precipitate, they are cooled at room temperature and finally, they are dried and washed for three times using deionized water.

Results and Discussion

Figure 1 shows that the IR spectrum has well-defined bands extended in the range from 500 to 790 cm^{-1} . These bands have been assigned to vibrational modes of the magnetite and the sharp peak centered in 590 cm^{-1} is originated from the Fe-O vibrations [48, 49], confirming the nature of the iron oxide nanoparticles. Furthermore, the rest of the absorption bands correspond to the organic species. The presence of groups H-H is observed at 892 cm^{-1} , single bonds of C-O of stretching are shown at 1051 as well in 1200 cm^{-1} . The presence of amide groups are observed at 1590 , 1662 and 3377 cm^{-1} . The bands at 1410 , 1710 , 2850 and 2920 cm^{-1} are attributed to the CH_3 umbrella mode in oleic acid, the stretching vibration of C=O, the asymmetric CH_2 stretch and the symmetric CH_2 stretch, respectively. Absorptions at 2923 and 2852 cm^{-1} correspond to stretching vibrations of C-H bonds. Besides, the broad band around 3400 cm^{-1} is assigned to stretching vibrations of N-H bonds and adsorbed water molecules. All these groups are related with the oleic acid, which demonstrates the covalent bridging of the oleate groups to the iron oxide surface [42]. These results allow us to assert that the nanoparticles obtained by this synthesis are coated with organic material [50].

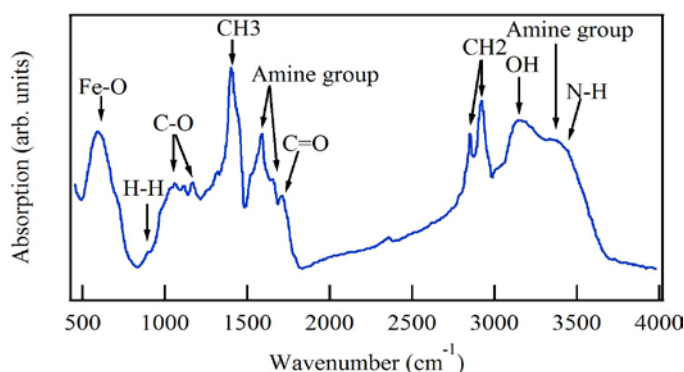


FIGURE 1. FTIR SPECTRA OF THE OBTAINED MAGNETITE NANOPARTICLES

Figure 2 shows the experimental x-ray diffractogram of the magnetite nanoparticles (dotted line) and computed diffractogram obtained from the refinement of their crystal structure (dark line). Refinement of the structure was done through the MAUD program [51], using as start pattern the iron diiron (III) oxide corresponding to the JCPDS card 88-0315 which has a cubic symmetry and $Fd\bar{3}m:1$ spatial group. From the refinement analysis it was shown that only the magnetite phase is present on the sample, and this has a lattice parameter of $8.3609 \pm 0.0006 \text{ \AA}$, and crystallite size of $33 \pm 2 \text{ nm}$. As is discussed below, the estimated average particle diameter by x-ray diffraction is consistent with the results determined by other techniques.

The measurement performed with LSD nanosizer equipment shows that the mean size of particles is 30.69 nm and a Gaussian adjusted to the experimental curve shows that the sigma value is 5.58 (see Fig 3), which indicates that particle size distribution is narrow due that in the interval $(-\sigma, \sigma)$ are contained the 68.2 % of the distribution.

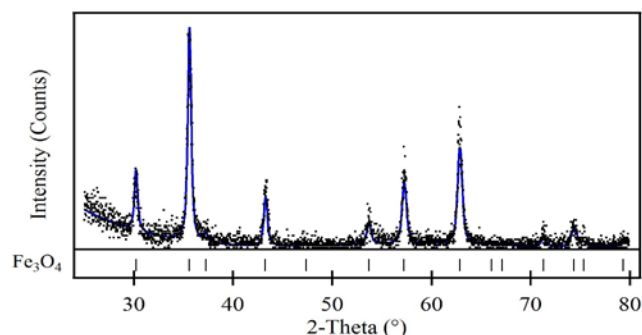


FIGURE 2. EXPERIMENTAL AND CALCULATED X-RAY DIFFRACTOGRAMS

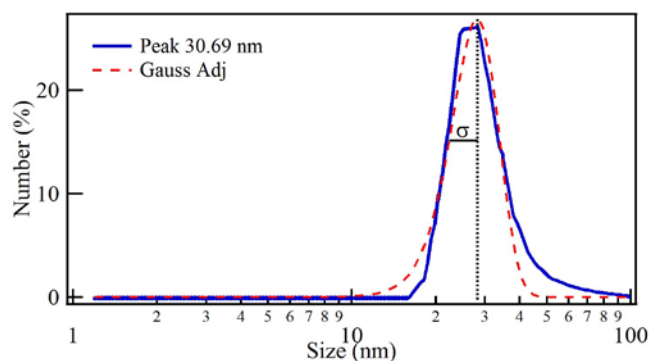


FIGURE 3. DISTRIBUTION SIZE MEASUREMENT

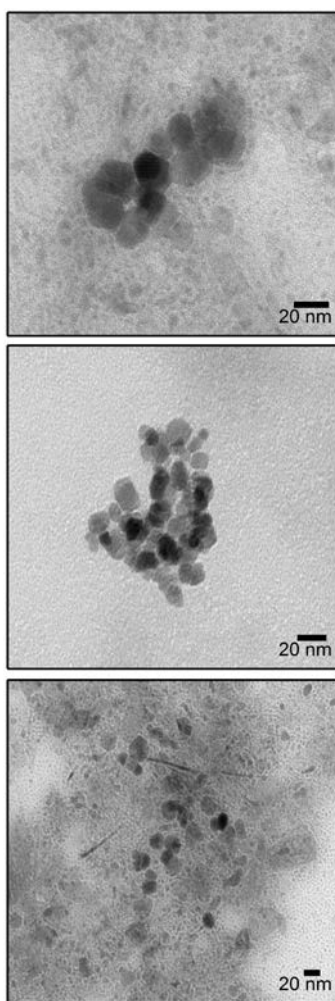


FIGURE 4. TEM IMAGE OF THE MAGNETITE NANOPARTICLES

The TEM observations presented in Figure 4 confirm the previous analysis of the size, distribution and shape of the nanoparticles. The micrograph shows that magnetite nanoparticles have about of 30 nm diameter with narrow size distribution and uniform shapes. By comparing this result with the obtained in x-ray (33 nm) and the obtained from LSD measurement (31 nm) we can affirm that by this method of preparation are obtained good-quality nanoparticles in easy way.

Here it is important to point out that using this method to produce magnetic nanoparticles translates in the possibility of obtaining small-sized nanoparticles while maintaining low temperature, in contrast, using similar methods keeping the low temperature, the obtained particle size can reach to 200 nm.

On the other way, the magnetic characterization made through the hysteresis loop, obtained from an AGM magnetometer shows that magnetite nanoparticles present a superparamagnetic behavior, which is desirable in many applications as hyperthermia or for magnetic pollutant recovering. The hysteresis curve is shown in Figure 5. In addition, the superparamagnetic behavior shown by the obtained nanoparticles indicates that the cover avoids their agglomeration and prevents that nanoparticles acquire a ferromagnetic behavior. In this manner, we can obtain pure magnetite nanoparticles that correspond to the boundary between superparamagnetic and single stable domain behavior with a coercivities around of 20 Oe, indicated by the particle size obtained by about 30 nm, in agreement with previous results [20].

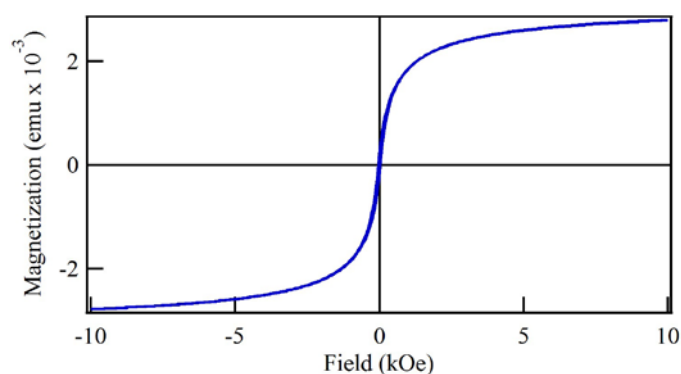


FIGURE 5. HYSTERESIS LOOP

Then, by comparing those preparation methods that require low temperatures to be recreated, such as the hydrothermal method with the method proposed in this work, the first ones, the minimum temperature used is 90°C during 12 hours and produce nanoparticles with high crystallinity, relatively high magnetic saturation and low coercivity values, but the grain size is about 200 nm [36, 52], while in our method, the nanoparticles have size about 30 nm with narrow size distribution, moreover they are superparamagnetic and have spherical uniform shape, plus, the temperature used to prepare them is of only 80°C.

Conclusions

In conclusion we have obtained magnetite nanoparticles at very low temperature, with previously non reported values by any similar method, we highlight that this method is a new and different way to produce magnetite nanoparticles. In this sense, we have established a single synthetic route to obtain superparamagnetic magnetite nanoparticles at lower temperature than those obtained by similar methods in which higher temperatures than 90°C are required. The modifications proposed here allow to obtain small-sized magnetite nanoparticles coated with organic material, this method having, as an advantage, the ease in which the nanoparticles are made.

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